Table I. Vibrational Data for Isotopomers of $Mo_2(O_2CCH_3)_4$ in the Range 450–150 cm^{-1} [a]

Raman				infrared	
$^{NA}Mo_2$	$^{NA}Mo_2$[b]	$^{92}Mo_2$[b]	$^{NA}Mo_2$-d_{12}	$^{NA}Mo_2$	$^{NA}Mo_2$-d_{12}
404	404	413	403		
				373	363
				353	343
				342	321
323	321	322	313, 310		
315	311	314	302		
301	298	299	293		
				311	285
				235	224
				230	220
204	200	200	201		
189	186	186	187		
				183	172

[a] NA = natural abundance. [b] Values were taken from ref 6. The excitation wavelength was 5145 Å, with the samples held at room temperature.

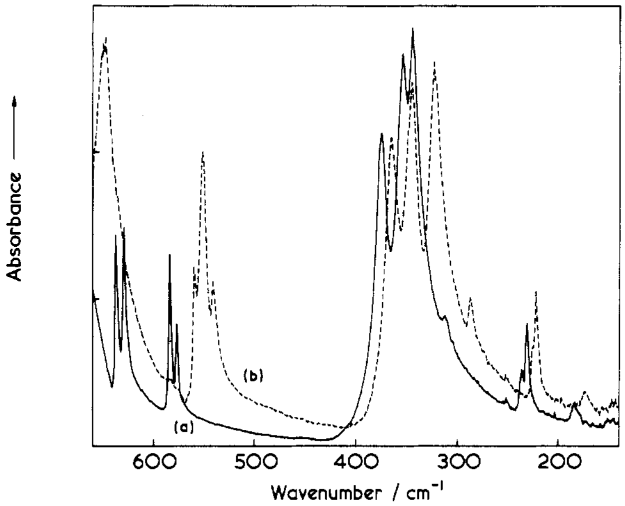

Figure 2. Far-infrared spectra of (a) $Mo_2(O_2CCH_3)_4$ and (b) $Mo_2(O_2CCD_3)_4$.

region shift by about 10 cm^{-1} to low wavenumbers. This is entirely consistent with the assignment of the 404-cm^{-1} band to the metal–metal stretch and the lower group of bands to the three Raman-active Mo–O stretching modes expected on a Mo_2O_8 vibrational model.[11] These Mo–O stretching modes shift by about 2 cm^{-1} to lower wavenumber on ^{92}Mo substitution of the natural molybdenum. The relative insensitivity of the two bands at 204 and 189 cm^{-1} to both ^{92}Mo[6] and deuterium substitutions suggests that they involve bending modes of the Mo_2O_8 skeleton. We also note that the insensitivity of the main progression-forming mode in the lowest energy electronic transition to deuteration[12] confirms that this progression is in the excited-state ν(Mo–Mo) mode, which has a wavenumber ca. 370 cm^{-1}.

The 80 K infrared spectrum (Figure 2) is consistent with these assignments. The three bands in the 373–342-cm^{-1} region shift 10–21 cm^{-1} to low wavenumber on deuteration. The shift of the member of this group with lowest wavenumber is much larger than would be expected on the basis of a pure Mo–acetate stretching mode in a Mo_2O_8 model (8 cm^{-1}), which suggests that some methyl rocking motion is also involved in this mode. This is not unexpected. Most of the higher wavenumber bands in the infrared and Raman spectra show appreciable shifts on deuteration, the smallest shifts being shown by the symmetric and asymmetric CO_2 stretching vibrations. There is no evidence in the infrared spectrum for a band at 404 cm^{-1}. This is consistent with the assignment of the Raman band at this wavenumber to ν(Mo–Mo), a fundamental that would be Raman- but not infrared-active in the D_{4h} point group to which the molecule belongs.

The effects of solid-state interactions on the number of Mo–O stretching modes active in the infrared spectra, on the appearance of new bands around 200 cm^{-1}, and on the substantial changes on deuteration in the 500–650-cm^{-1} region will be detailed in a separate study.[13]

Conclusion

The results of this study indicate that deuteration of the carboxylate group may provide a useful, low-cost alternative to ^{18}O- and metal-isotope-substitution experiments for the assignment of metal–metal stretching vibrations in dimeric tetracarboxylates.

Acknowledgment. We thank the University of London Intercollegiate Research Service for access to the Raman and infrared spectrometers.

Registry No. $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Mo_2(O_2CCD_3)_4$, 61483-82-7; D_2, 7782-39-0.

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Synthesis and Molecular Structure of $Os_2(\mu\text{-}PPh_2)(\mu\text{-}I)(CO)_6$. High-Yield Syntheses of $Os_2(\mu\text{-}I)_2(CO)_6$ and $Os_2I_2(CO)_8$

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Received December 26, 1985

The binuclear phosphido-bridged osmium complexes $Os_2(CO)_6(\mu\text{-}X)(\mu\text{-}PPh_2)$ (**1**) and $Os_2(CO)_6(\mu\text{-}PPh_2)_2$ (**2**) are interesting compounds because the μ-halide functionality of **1** should allow the preparation of derivatives with organic ligands and **2** is analogous to the well-studied complex $Fe_2(\mu\text{-}PPh_2)_2(CO)_6$.[1,2] The relative chemical inertness of Os in **2**, as compared to Fe, should permit the preparation of intermedites that have escaped detection or isolation in the Fe system.[1,2]

The logical approach to the synthesis of phosphido-bridged compounds containing halide ligands is the metathesis reaction between $LiPPh_2$ and binuclear metal halide complex.[3,4] For the preparation of the desired Os_2 complexes **1** and **2**, potentially useful synthetic reagents are the halide complexes $Os_2I_2(CO)_8$ (**3**) and $Os_2(\mu\text{-}I)_2(CO)_6$ (**4**).[5,6] Herein we describe the synthesis of **1** (X = I) from **4** and its structural characterization as well as some aspects of its reactivity. Also described are attempts to prepare the bis(phosphido)-bridged complex **2**. During the course of these studies we optimized the syntheses of **3** and **4**, and those details are also reported.

Results

The reactions successfully carried out in this work are summarized in Schemes I and II.

High-Yield Syntheses of $Os_2I_2(CO)_8$ (3) and $Os_2(\mu\text{-}I)_2(CO)_6$ (4). The title complexes can be prepared by the thermal reaction of $Os_3(CO)_{12}$ with I_2 in toluene.[5] We have found that the temperature at which the reaction is conducted is critical in deter-

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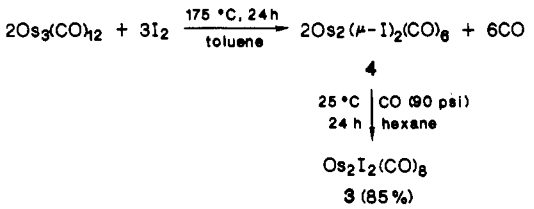
Scheme I



Scheme II

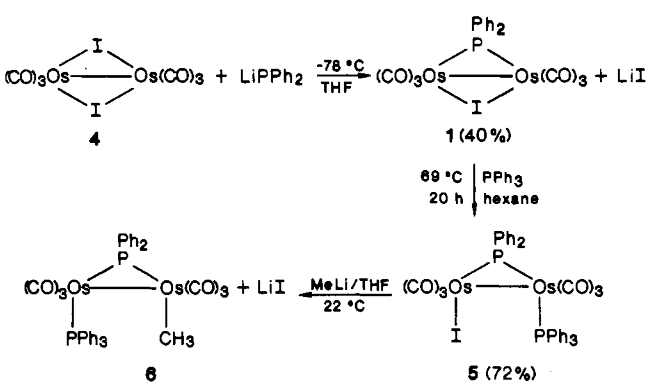


Table I. Crystal Parameters, Data Collection, and Refinement Results for $[Os_2(\mu\text{-}PPh_2)(\mu\text{-}I)(CO)_6]$ (**1**)

Crystal Parameters	
formula	$Os_2C_{18}H_{10}IO_6P$
fw	860.5
cryst syst	monoclinic, $P2_1/c$
a, Å	15.765 (3)
b, Å	8.075 (1)
c, Å	17.610 (4)
β, deg	110.44 (2)
V, Å^3	2100.6 (8)
Z	4
ρ(calcd), g cm^{-3}	2.72
μ(Mo Kα), cm^{-1}	136.6
color	yellow
cryst dimens, mm	0.30 × 0.31 × 0.33
temp, °C	22
Data Collection	
diffractomer	Nicolet R3
radiation (λ, Å)	Mo Kα (0.71073)
monochromator	graphite
scan range, deg	$4 \leq 2\theta \leq 48$
scan type	ω
scan speed, deg min^{-1}	var 4-20
no. of stds/no. of rflns	3/197 (no decay)
no. of rflns collected	3303 ($\pm h,+k,+l$)
tranmission max/min	0.076/0.050
Refinement	
no. of unique rflns	3297
R(int), %	3.01
no. of unique rflns with $F_o \geq 3\sigma(F_o)$	2965
R_F/R_{wF},[a] %	4.47/5.23
GOF	1.35
g	0.0008
highest peak in final diff map, e Å^{-3}	1.10 (1.11 Å for Os(2))

[a] $w^{-1} = \sigma^2(F_o) + |g|(F_o)^2$; $R_F = \sum[|F_o| - |F_c|]/\sum|F_o|$; $R_{wF} = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; GOF $= [\sum w(F_o - F_c)^2/(N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

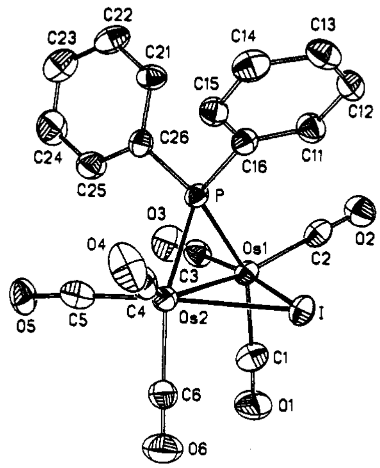


Figure 1. ORTEP drawing of $Os_2(\mu\text{-}PPh_2)(\mu\text{-}I)(CO)_6$ (**1**). Thermal ellipsoids are drawn at the 40% probability level.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for **1**

atom	x	y	z	U_{iso}[a]
Os(1)	2864.5 (3)	7976.1 (5)	624.2(3)	39 (1)
Os(2)	1958.3 (3)	10160.6 (5)	−621.8 (2)	37 (1)
I	1002.4 (5)	8173.7 (9)	72.2 (5)	48 (1)
P	2722 (2)	10852 (3)	758 (2)	38 (1)
O(1)	2668 (9)	5027 (13)	−520 (7)	90 (6)
O(2)	3074 (7)	6532 (12)	2300 (6)	69 (4)
O(3)	4867 (6)	8241 (15)	925 (7)	89 (5)
O(4)	563 (7)	12940 (13)	−1150 (6)	79 (5)
O(5)	3204 (6)	11845 (12)	−1369 (5)	66 (4)
O(6)	1393 (7)	7724 (14)	−2043 (6)	85 (5)
C(1)	2747 (8)	6065 (16)	−84 (8)	61 (5)
C(2)	3014 (8)	7070 (14)	1686 (8)	49 (5)
C(3)	4113 (8)	8145 (17)	820 (7)	58 (5)
C(4)	1059 (8)	11874 (17)	−9976 (7)	56 (5)
C(5)	2733 (7)	11224 (16)	−1053 (7)	52 (4)
C(6)	1609 (8)	8597 (17)	−1529 (7)	55 (5)
C(11)	1813 (8)	10843 (16)	1884 (7)	53 (5)
C(12)	1227 (9)	11500 (16)	2238 (8)	62 (6)
C(13)	840 (8)	12995 (16)	2016 (7)	56 (5)
C(14)	1048 (8)	13925 (16)	1433 (8)	58 (5)
C(15)	1621 (8)	13253 (14)	1071 (7)	47 (5)
C(16)	2008 (7)	11710 (14)	1288 (7)	42 (4)
C(21)	3944 (8)	13102 (14)	1802 (7)	49 (5)
C(22)	4686 (8)	14073 (17)	2057 (8)	65 (5)
C(23)	5288 (9)	14140 (19)	1618 (8)	71 (6)
C(24)	5106 (9)	13165 (21)	947 (9)	78 (7)
C(25)	4341 (9)	12183 (18)	698 (8)	62 (5)
C(26)	3730 (7)	12160 (14)	1090 (7)	44 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

mining the yields of **3** and **4** which can be isolated from the reaction mixture. Careful maintenance of the temperature between 175 and 180 °C using either benzene or toluene as solvent gave yields of **4** as high as 95% (Scheme I). Alternatively, if the reaction was run in the 165–175 °C temperature range, mixtures of **3** (30%) and **4** (70%) were obtained. This mixture can be conveniently separated by chromatography on Florisil.[5] Also, any **3** that is formed can be converted into **4** by refluxing the complex in heptane to induce CO loss.[6] We have also found that the reverse of this latter reaction readily occurs since carbonylation of **4** gives **3** in good yield (Scheme I).

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Table III. Selected Bond Distances and Angles for $Os_2(\mu\text{-}PPh_2)(\mu\text{-}I)(CO)_6$

	(a) Bond Distances, Å		
Os(1)–I	2.756 (1)	Os(2)–C(5)	1.86 (1)
Os(2)–I	2.761 (1)	Os(2)–C(6)	1.96 (1)
Os(1)–Os(2)	2.789 (1)	C(1)–O(1)	1.11 (1)
Os(1)–P	2.353 (3)	C(2)–O(2)	1.14 (1)
Os(2)–P	2.371 (3)	C(3)–O(3)	1.14 (1)
Os(1)–C(1)	1.95 (1)	C(4)–O(4)	1.13 (1)
Os(1)–C(2)	1.94 (1)	C(5)–O(5)	1.18 (1)
Os(1)–C(3)	1.88 (1)	C(6)–O(6)	1.10 (1)
Os(2)–C(4)	1.92 (1)		
	(b) Bond Angles, deg		
Os(1)–I–Os(2)	60.7 (0)	C(2)–Os(1)–C(3)	94.8 (5)
Os(1)–P–Os(2)	72.4 (1)	C(4)–Os(2)–C(5)	92.9 (6)
Os(1)–Os(2)–I	59.5 (0)	C(4)–Os(2)–C(6)	103.6 (5)
Os(2)–Os(1)–I	59.7 (0)	C(5)–Os(2)–C(6)	90.1 (6)
Os(1)–Os(2)–P	53.5 (1)	Os(1)–C(1)–O(1)	177 (1)
Os(2)–Os(1)–P	54.1 (1)	Os(1)–C(2)–O(2)	178 (1)
I–Os(1)–P	81.4 (1)	Os(1)–C(3)–O(3)	179 (1)
I–Os(2)–P	81.0 (1)	Os(2)–C(4)–O(4)	176 (1)
C(1)–Os(1)–C(2)	105.7 (5)	Os(2)–C(5)–O(5)	176 (1)
C(1)–Os(1)–C(3)	91.9 (6)	Os(2)–C(6)–O(6)	179 (1)
	(c) Dihedral Angle, deg		
[Os(1)–Os(2)–P]–[Os(1)–Os(2)–I]		102.1 (2)	

Synthesis of $(CO)_3\overline{Os(\mu\text{-}I)(\mu\text{-}PPh_2)Os}(CO)_3$ (1). This compound can be prepared directly by reaction of complex **4** with $LiPPh_2$ (Scheme II). Complex **1** has been spectroscopically characterized and fully defined by an X-ray diffraction study; see below. The ^{31}P NMR spectrum of **1** shows a single resonance at δ 48.0 due to the μ-PPh_2 ligand with the downfield position of this signal in agreement with the presence of a metal–metal bond (2.789 (1) Å).[7]

Surprisingly, complex **1** does not further react with excess $LiPPh_2$ to form the expected bis(phosphido)-bridged complex **2**, and **1** is recovered largely unchanged from such reactions. On several occasions, reaction of $Os_2(\mu\text{-}I)_2(CO)_6$ with excess $LiPPh_2$ did give very small amounts (~6 mg) of a material identified as **2** by its spectroscopic data (see Experimental Section).

Crystal and Molecular Structure of 1. An ORTEP drawing of complex **1** is shown in Figure 1, and pertinent crystallographic details are set out in Tables I–III. The two Os atoms are bridged by μ-PPh_2 and μ-I ligands with each Os further coordinated by three CO's. The $Os_2(\mu\text{-}P)(\mu\text{-}I)$ core of **1** is bent with a [Os(1)–Os(2)–P]–[Os(1)–Os(2)–I] dihedral angle of 102.1 (2)°. This bending is slightly greater than that found in its isostructural analogue $Fe_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(CO)_6$, which has a dihedral angle of 101.5°,[8] but less than that found in $Os_2(\mu\text{-}I)_2(CO)_6$ (113.9°).[6] The Os–Os bond distance of 2.789 (1) Å is characteristic of a single bond between these metals. For comparison the average Os–Os distance in $Os_3(CO)_{12}$ is 2.8771 (27) Å,[9] and in $Os_2(\mu\text{-}I)_2(CO)_6$ the Os–Os distance is 2.722 (2) Å.[6] The latter compound has a geometry similar to that of **1**, and replacing one μ-I ligand by the μ-PPh_2 ligand in forming **1** resulted in a 0.067-Å lengthening of the Os–Os bond.

Displacement of the μ-I Ligand in 1 to a Terminal Position by Addition of PPh_3. Complex **1** reacts with PPh_3 in refluxing hexane by displacing the μ-I ligand to a terminal position and adding PPh_3 to the adjacent Os (Scheme II). Complex **5** was isolated in good yield and spectroscopically characterized. Its mass spectrum showed the parent ion and fragment ions corresponding to progressive loss of 6 CO's. Two doublets at δ 83.2 (J_{P-P} = 107.4 Hz) and δ −3.4 were observed in its ^{31}P NMR spectrum which were respectively assigned to the μ-PPh_2 and PPh_3 ligands. The downfield position of the μ-PPh_2 resonance implies the presence of a metal–metal bond in **5** as required by the 18-e rule.

Reaction of 1 and 5 with Methyllithium. The bridging halide ligand in complex **1** has proven difficult to replace directly. Treatment of complex **1** with MeLi or $Li[BHEt_3]$, for example, gave fragmentation products rather than the expected methyl and hydride complexes. However, the bridging iodide can be activated by displacement to a terminal position by addition of PPh_3 to form complex **5**. Preliminary reactivity studies indicate that the iodide ligand in **5** can be readily displaced by organic nucleophiles. For example, reaction of complex **5** with MeLi gave complex **6**, in which the iodide ligand was replaced by a methyl group (Scheme II). Complex **6** was isolated in modest yield and spectroscopically characterized. Its mass spectrum showed the parent ion at m/z 1014 (^{192}Os), and a characteristic methyl resonance was observed at δ 0.22 (d, J_{H-P} = 8.3 Hz) in its ^1H NMR spectrum. The ^{31}P NMR spectrum of **6** shows two doublets at δ −2.6 (J_{P-P} = 92.6 Hz) and δ 92.4 due respectively to the PPh_3 ligand and μ-PPh_2 ligands. The downfield position of the latter implies the presence of a metal–metal bond in **6** as required by the 18-e rule.

Experimental Section

The reagents $Os_3(CO)_{12}$[10] and $LiPPh_2\cdot diox$[11] (diox = dioxane) were prepared by literature procedures. PPh_2H (Strem), *n*-BuLi, MeLi, PPh_3 (Aldrich), and CO (Airco) were used as received without further purification. Unless specified otherwise, all manipulations were performed by using standard Schlenk techniques under an atmosphere of prepurified N_2. Complexes **3**[6] and **4**[5] were prepared by improved procedures.[12,13]

Synthesis of $Os_2(\mu\text{-}PPh_2)(\mu\text{-}I)(CO)_6$ (1). An orange solution of $LiPPh_2$.diox (330 mg, 1.18 mmol) in 90 mL of THF was added dropwise over 1.75 h to a stirred solution of complex **4** (940 mg, 1.17 mmol) in 140 mL of THF at −78 °C. After the mixture was stirred for 48 h, the solvent was removed from the orange-red solution by rotary evaporation leaving a red oil. The oil was dissolved in a minimum of CH_2Cl_2 and adsorbed onto 2 g of Florisil. This was loaded at the top at a 24 in. × $^3/_4$ in. glass chromatography column. Elution with hexane afforded a yellow band of unreacted **4** followed by a yellow band of complex **1**. Slow evaporation of hexane (4 days) from the latter band afforded the desired compound as an air-stable microcrystalline solid in 40% yield (403 mg, 0.47 mmol). Anal. Calcd for $C_{18}H_{10}IO_6Os_2P$: C, 24.11; H, 1.16. Found: C, 24.46; H, 1.44. IR (hexane): ν_{CO} 2084 (s), 2053 (vs), 2008 (s), 1989 (s), 1979 (w) cm^{-1}. MS (EI): m/z 864 (M^+, ^{192}Os), 836 (M^+ − CO), 808 (M^+ − 2CO), 780 (M^+ − 3CO), 752 (M^+ − 4CO), 724 (M^+ − 5CO), 696 (M^+ − 6CO).

On several occasions reaction of $Os_2(\mu\text{-}I)_2(CO)_6$ (401 mg, 0.500 mmol) with excess $LiPPh_2\cdot diox$ (280 mg, 1.000 mmol) in THF (75 mL) at room temperature (~25 °C) led to the isolation of a small amount of (~6 mg) of $Os_2(\mu\text{-}PPh_2)_2(CO)_6$. The compound, a yellow crystalline solid, was obtained as the second band that eluted with hexane in the chromatography of **1** on Florisil. IR (hexane): ν_{CO} 2072 (s), 2043 (vs), 2004 (vs), 1975 (vs), 1966 (m) cm^{-1}. MS (EI): m/z 922 (M^+, ^{192}Os).

Synthesis of $Os_2(\mu\text{-}PPh_2)(I)(CO)_6(PPh_3)$ (5). A 100-mL Schlenk flask was charged with complex **1** (420 mg, 0.488 mmol), PPh_3 (310 mg,

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(12) Synthesis of $Os_2(\mu\text{-}I)_2(CO)_6$ (**4**): A 300-mL Carius tube was charged with $Os_3(CO)_{12}$ (0.45 g, 0.5 mmol), I_2 (0.19 g, 0.75 mmol), and 25 mL of toluene. The Carius tube was evacuated to ca. 0.01 torr, wrapped with wire mesh, and heated in an oil bath at 175–180 °C behind a safety shield for 24 h. After cooling to room temperature, the tube was opened in air and the solvent removed to give complex **4** as an air-stable orange microcrystalline solid in 95% yield (0.57 g, 0.71 mmol; mp 87–89 °C). IR (hexane): ν_{CO} 2089 (m), 2069 (s), 2016 (s), 2010 (s), 2004 (w) cm^{-1}. MS (EI): *m*-*z* 806 (M^+, ^{192}Os).

(13) Synthesis of $Os_2I_2(CO)_8$ (**3**): A 100-mL Fischer–Porter bottle was charged with complex **4** (1.25 g, 1.56 mmol) and hexane (50 mL) in air. The reaction vessel was then pressurized with 90 psi of CO, vented, and repressurized with CO. The solution was stirred at room temperature for 24 h, during which time yellow microcrystalline **3** precipitated. After the pressure bottle was vented, the product was collected by filtration, washed with several small portions of hexane, and air-dried. This gave complex **3** in 55% yield (0.74 g, 0.86 mmol; mp 133–136 °C). Additional product was obtained after chromatography of the filtrate on a 4 in. × $^3/_4$ in. Florisil column. After the filtrate was loaded on the column, elution with *n*-hexane gave a small yellow band of complex **4**. Further elution with 1:1 (v/v) *n*-hexane/CH_2Cl_2 gave a yellow band of complex **3**. The solvent was removed from the latter band on a rotary evaporator to yield an additional 30% (0.40 g, 0.47 mmol) of **3**. IR (hexane): ν_{CO} 2113 (s), 2076 (s), 2064 (vs), 2059 (vs), 2049 (s), 2030 (s) cm^{-1}. MS (EI): *m*-*z* 862 (M^+, ^{192}Os).

1.18 mmol), and 40 mL of *n*-hexane in air. The solution was refluxed under nitrogen with stirring for 16 h. During this time, a yellow solid gradually precipitated. This was collected by filtration, washed with several small portions of hexane, and air-dried to give complex **5** as an air-stable yellow microcrystalline solid in 72% yield (395 mg, 0.352 mmol). The infrared spectrum of the filtrate showed only unreacted starting material. Anal. Calcd for $C_{36}H_{25}IO_6Os_2P_2$: C, 38.50; H, 2.23. Found: C, 39.06; H, 2.49. IR (CH_2Cl_2): ν_{CO} 2089 (w), 2056 (s), 2012 (vs), 1994 (ssh), 1968 (m sh) cm^{-1}. MS (EI): *m/z* 1126 (M^+, ^{192}Os), 1098 ($M^+ - CO$), 1070 ($M^+ - 2CO$), 1042 ($M^+ - 3CO$), 1014 ($M^+ - 4CO$), 986 ($M^+ - 5CO$), 960 ($M^+ - 6CO$).

Synthesis of $Os_2(\mu\text{-}PPh_2)(CH_3)(CO)_6(PPh_3)$ (6). A 100-mL Schlenk flask was charged with complex **5** (54 mg, 0.053 mmol), 20 mL of THF, and MeLi (45 μL of a 1.2 M Et_2OH solution). The reaction mixture was stirred for ca. 5 min at room temperature after which time the solvent was removed under vacuum and the residue extracted with several small portions of benzene. The benzene was removed by rotary evaporation to yield complex **6** as a yellow oil. Attempts to crystallize this oil were not successful. The product was shown to be pure by solution infrared spectroscopy and subsequently characterized by ^{31}P NMR, ^1H NMR, and mass spectroscopy. IR (THF): ν_{CO} 2074 (w), 2035 (s), 1997 (vs), 1964 (s), 1946 (m) cm^{-1}. MS (EI): *m/z* 1014 (M^+, ^{192}Os).

X-ray Diffraction Study of 1. A crystal of **1** grown from hexane was mounted on a glass fiber. Preliminary photographic work and systematic absences uniquely identified the space group as $P2_1/c$. The unit-cell parameters reported in Table I were obtained from the least-squares fit of the angular settings of 25 reflections ($20° \leq 2\theta \leq 30°$). An empirical absorption correction based on ψ-scans of seven close-to-axial reflections was applied to the intensity data.

Direct methods (SOLV) revealed the Os and I atom locations. The remainder of the non-hydrogen atoms were located in subsequent difference Fourier syntheses. The model used in the final refinement by a blocked-cascade routine included all non-hydrogen atoms as anisotropic contributions and hydrogen atoms as idealized (d(C–H) = 0.96 Å) isotropic contributions. The final data/parameter ratio was 11.71/1. The mean Δ/σ of the final cycle was 0.023, and the slope of a normal probability plot was 1.236. All programs and scattering factors were obtained from the SHELXTL (version 4.1) and P3 program packages (Nicolet Corp., Madison, WI). Final atomic coordinates are given in Table III.

Acknowledgment. The National Science Foundation (Grant CHE8501548) is gratefully acknowledged for support of this research and for contributing to the purchase of the X-ray diffractometer at the University of Delaware. A.W.H. thanks Loyola University of Chicago for summer support through a Faculty Development Research Grant.

Registry No. **1**, 102851-52-5; **3**, 22587-71-9; **4**, 22391-77-1; **5**, 102851-54-7; **6**, 102851-55-8; $Os_2(\mu\text{-}PPh_2)_2(CO)_6$, 102851-53-6; $Os_3(CO)_{12}$, 15696-40-9; Os, 7440-04-2.

Supplementary Material Available: Tables of anisotropic temperature factors, complete bond lengths and angles, and calculated hydrogen atom positions for **1** (2 pages). Ordering information is given on any current masthead page.

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Oxide-Dependent Deposition and H_2-Promoted Aggregation of Organorhodium Complexes

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Received November 13, 1985

We have recently described the chemistry of organorhodium complexes deposited on a variety of oxide surfaces, and we have demonstrated that variation in non-oxide ligation about the metal center can be used to control reactivity of the bound complex.[1] Although in previous work we had noted that a variety of oxides could be used for chemical attachment of organorhodium complexes,[2] we had not extensively studied how variation in the oxide itself affects the structure or reactivity of complexes bound thereto, and deposition control was attained only by adjusting *total* content of hydroxyl groups on the oxide. The more subtle notion was not considered that *relative* locations might vary of reactive hydroxyl groups on oxides of different structure, although this distribution of reactive sites would control deposition of 1 equiv of an organometallic with regard to another. Silica and alumina are among the most commonly used oxides for chemical attachment to reactive organometallic complexes,[3] and we have found that an interesting oxide-dependent deposition phenomenon distinguishes these two materials: although for both we have utilized samples containing a large excess of reactive hydroxyl groups relative to total rhodium deposited, we note that, for silica, deposition of rhodium complexes occurs selectively to generate *dimers*; on alumina (of comparable total surface hydroxyl group concentration), *monomers* are formed. In the course of these studies we also have found that hydrogen, a typical reagent for "activation" of oxide-bound organometallic species, enables migration of surface-"bound" organorhodium complexes and fosters the conversion of deposited "weak dimers" to aggregates.

Experimental Section

Infrared, UV-vis, and mass spectra were recorded on Digilab FTS-20C, Hewlett Packard, and AEI MS9 instruments, respectively. GC and GC/MS spectra were recorded by Hewlett Packard 5840A and 5992B instruments respectively. IR spectra of oxide-bound complexes were recorded by using self-supporting pressed disks with unreacted oxide samples in the reference beam. Oxides used were Aerosil 300 (SiO_2) and Aluminoxid C (Al_2O_3), Degussa, and were dried in vacuo prior to use. All reactions were performed at room temperature under N_2 except where noted otherwise.

Preparation of $Rh(C_3H_5)(CO)_2$ (1). $[Rh(CO)_2Cl]_2$ (0.25 g) was dissolved in dry Et_2O (15 mL) under N_2. The reaction mixture was cooled to 0 °C, and 1 equiv of C_3H_5MgCl/Et_2O was added dropwise. The reaction mixture was stirred for 30 min, and the solvent was then removed in vacuo (ca. 30 torr). The product was extracted with *n*-pentane and obtained by evacuation; it was sublimed before use.

Deposition of 1 onto Oxide Supports. Sublimed **1** was dissolved in pentane; the concentration of the solution was determined by UV–visible spectroscopy from a calibrated plot of concentration vs. absorbance at λ = 388 nm, and a measured amount of reactive solution was added to a slurry of oxide in pentane under N_2. After 24 h of stirring, excess **1** was removed by washing with pentane and was quantified by UV–visible spectroscopy.

Treatment of dried SiO_2 (Degussa Aerosil 300; dried at 200 °C (0.02 torr), 24-h period) with a pentane solution of $Rh(C_3H_5)(CO)_2$ for 24 h resulted in an off-white solid showing IR absorptions at 2107 (sh), 2091 (s), and 2033 (s) cm^{-1}. Treatment of dried Al_2O_3 (Aluminoxid C; dried at 200 °C (0.02 torr), 24–h period) with a pentane solution of $Rh(C_3H_5)(CO_2)_2$ for 24 h resulted in a pale yellow solid showing IR absorptions at 2091 (s) and 2021 (s) cm^{-1}.

Preparation of ^{13}CO-Enriched Samples. A mixture of $^{12}CO/^{13}CO$ was made up and this same mixture used for all the following reactions. The mixture contained a large excess of CO relative to the rhodium complexes.

(a) ^{13}CO-Enrichment of $[Rh(CO)_2Cl]_2$. $[Rh(CO)_2Cl]_2$ (0.5 g) was dissolved in hexane (50 mL), the solution was degassed by freeze–thaw cycles and frozen, the $^{12}CO/^{13}CO$ mixture was introduced, and the vessel was then sealed. The reactants were warmed to room temperature and stirred for 4 h. The solvent was removed in vacuo and the product

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